An MO-Theoretical Study of the Decomposition of Hydroperoxides by Sulfonium Compounds and Some Nucleophiles

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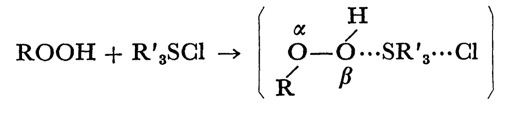
The decomposition reactions of hydroperoxides (ROOH) by sulfonium compounds or some nucleophiles (sulfides, phosphites, and transition metal ions) were treated by the extended Hückel method, augmented by the use of *d*-orbitals. We obtained serveral findings. First, ROOH was more reactive to nucleophiles and was energetically more stable than $(ROOH)_2$. Second, the order of the ability for the ROOH decomposition, sulfonium compounds $\gg$ sulfides $>$ phosphites $\gtrsim$ thiophene, was in good agreement with that of the AO populations of the nonbonding lone pair orbitals of the above compounds. Third, the distinguished ability of the sulfonium compound may be attributed to the contribution of the partially-occupied sulfur *d*-orbitals, in particular, the lowest unoccupied d_{z^2}-orbital; in the ROOH decomposition, these orbitals interact with the lowest unoccupied antibonding $p\sigma$-orbital of the O-O in ROOH at the O_β atom in the direction of the O-O axis. Finally, it was concluded that the sulfur *d*-orbitals contribute to the long-range interaction (S-$O_\beta > 3.0$ Å) between ROOH and sulfonium compounds.

The thermal[1] and catalytic[2] decompositions of hydroperoxides have been widely investigated by taking notice of the decomposition mechanism. Some chemical properties of hydroperoxides have thus been unveiled such as the kinds of homolytic or heterolytic decomposition products,[1-3] the bond-dissociation energies of the oxygen-oxygen bond[4,5] (including those of alkoxyl radicals[6]), and the association of hydroperoxides.[7,8] On the other hand, some theoretical studies of the electronic structures of hydroperoxides can be found in Refs. 9, 10, and 11, and more recently in Ref. 12. These studies suggest that most hydroperoxides possess the lowest unoccupied antibonding $p\sigma$-type-orbital of the O-O bond and that the bond can easily be cloven by nucleophiles such as low-valent metal ions,[13,14] sulfides[15] and phosphites.[16]

In our previous paper,[17] which referred to the remarkable ability of sulfonium compounds in the catalytic decomposition of hydroperoxides, a presumption was made that the partially occupied d_{z2} and/or d_{xz} (or d_{yz}) orbitals[18,19] play an important role in the scission of the O–O bond as follows:



$$ROOH + R'_3SCl \rightarrow \left(\overset{\alpha}{O}\!-\!\overset{H}{\underset{\beta}{O}}\cdots SR'_3\cdots Cl \right)$$

$$\rightarrow RO\cdot + \cdot OH + R'_3SCl$$

(R, R' = alkyl or aryl)

The electron transferred from the sulfonium part to the O–O bond through the sulfur *d*-orbitals increases the antibonding character of the O–O bond and promote the scission.

The present study intends to elucidate the role of the *d*-orbitals of sulfonium compounds in the catalytic decomposition of hydroperoxides, comparing their role with those of the nonbonding lone pair orbitals of sulfides and phosphites.

Methods of Calculation

Four systems were investigated in this work: (a) hydroperoxides, ROOH (R=H, CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, t-C_4H_9, and $C_6H_5C(CH_3)_2$), (b) dimeric hydroperoxides $(ROOH)_2$ (R=H, CH_3, and t-C_4H_9), (c) trimethylsulfonium chloride ($(CH_3)_3SCl$) and some nucleophiles ($(CH_3)_2S$, $(C_6H_5)_2S$, $(CH_3O)_3P$, and $(C_2H_5O)_3P$, and (d) the interaction of CH_3OOH with $(CH_3)_3SCl$, $(CH_3)_2S$ or $(CH_3O)_3P$. In the case of (d), CH_3OOH was used for the simplicity of computation.

The orbital exponents and the Coulomb integrals ($H_{\mu\mu}$) were supplied by Clementi[20] and Jaffé[21,22] respectively. Especially, the $H_{\mu\mu}$ values of the oxygen

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$2p$-orbital and the sulfur $3d$-orbital were taken to be -13.61 eV and -7.00 eV[23] respectively. The resonance integrals ($H_{\mu\nu}$) were evaluated by the Wolfsberg-Helmholtz approximation[24]:

$$H_{\mu\nu}=0.875(H_{\mu\mu}+H_{\nu\nu})S_{\mu\nu}$$

where $S_{\mu\nu}$ is the overlap integral between AO's.

The orbital contour diagrams were calculated by the use of Slater's AO functions.[26]

Experimental

The decomposition reaction of cumene hydroperoxide was carried out in the following way: cumene hydroperoxide (22.5 mmol) in cumene (50 m*l*) was vigorously stirred in the presence of sulfonium chloride or a nucleophile (a sulfide, a phosphite, or a transition metal salt), mainly at 80°C for 4.0 hr. Then, the reaction mixture was pipetted out and submitted to analyses of the decomposition products, acetophenone (AP), dicumyl peroxide (DCP), α-cumyl alcohol (CA), and the residual cumene hydroperoxide (CHP). The analytical treatment was carried out in accordance with the method mentioned previously.[17]

Results and Discussion

Electronic Structures of Hydroperoxides. Before discussing the interaction between hydroperoxides (ROOH) and sulfonium compounds (R'_3SCl), the electronic structures of the former should be reviewed. ROOH is characterized by its lowest unoccupied (LU) antibonding $p\sigma$-type O–O bond. Considering that the atom population of the O_β in $RO_\alpha O_\beta H$ is larger than that of the O_α, as is indicated in Fig. 1, such nucleophiles as sulfides and phosphites will interact with ROOH from the O_β side in the direction of the O–O axis.[12] In the case of sulfonium compounds, the interaction will occur between the d-orbitals of the central sulfur and the O–O $p\sigma$-orbital in the same way mentioned above, perhaps because substituents of the sulfonium compound (named R′) sterically hinder the approach of the compound from the O_α side.[17] The characteristic nature of the O–O bond in ROOH is reflected in the orbital contour diagrams for the LU MO of ROOH ($R=CH_3$) (see Fig. 2).

It is of interest here to discuss which structure of ROOH, monomer or dimer, is energetically more plausible. The total energies listed in Table 1 demonstrated that the ROOH monomer is preferable for the structure of ROOH, especially at low concentrations of the hydroperoxide. In regard to the reactivity of ROOH to nucleophilic reagents, the partial AO bond population of the O–O in the LU MO ($1/2N_{p\sigma}^{LU}$) can be utilized as a reactivity index since the O–O bond is mainly conposed of the $p\sigma$-orbital of the O–O (see Table 1). The value of $1/2N_{p\sigma}^{LU}$ in Table 1 suggests that ROOH is more reactive than $(ROOH)_2$. On the basis of the above discussions, the monomer structure of ROOH seems to be the more plausible structure from the standpoints of both the energetic stability and the reactivity to nucleophiles.

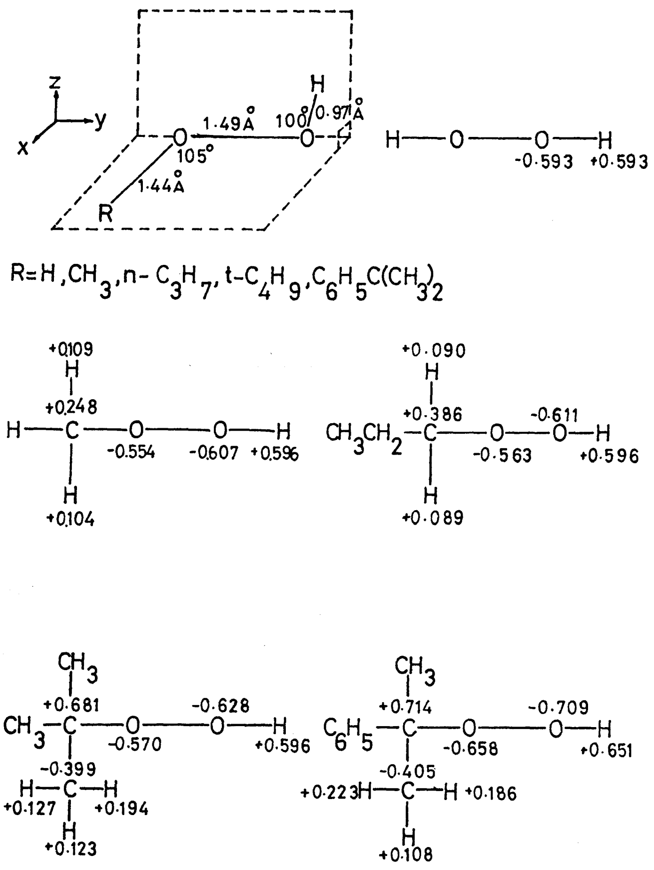

Fig. 1. Atomic charges of some hydroperoxides.

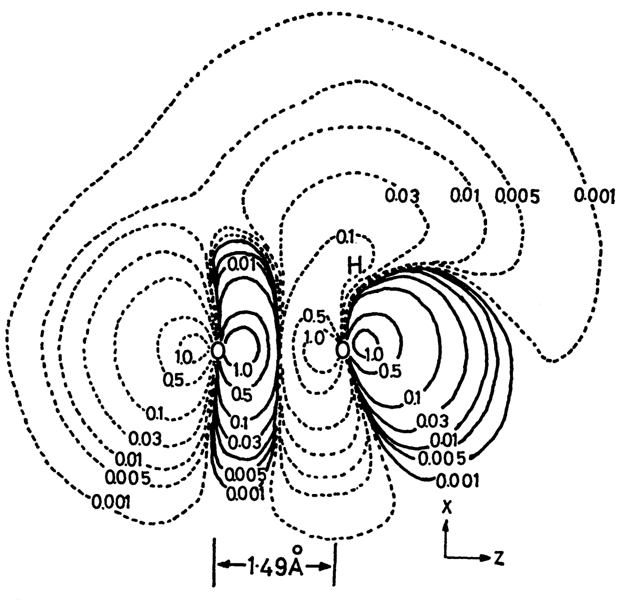

Fig. 2. Orbital contour of CH_3OOH in the LU MO. (the solid and broken lines stand for the positive and negative MO signs, respectively.)

Decomposition of Cumene Hydroperoxide by Sulfonium Compounds and Some Nucleophiles. It is of interest also to discuss the abilities of sulfonium compounds and some nucleophiles with regard to the decom-

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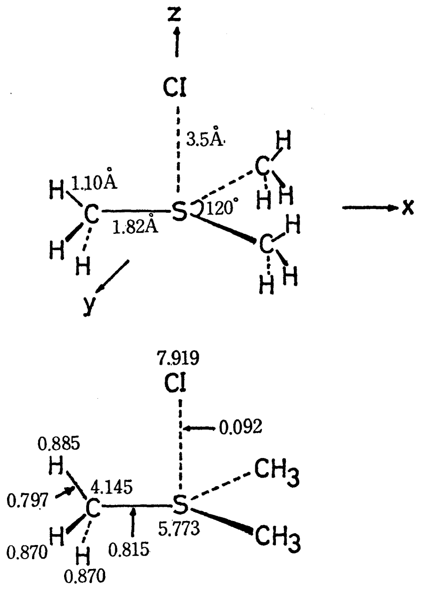
TABLE 1. SOME ELECTRONIC PROPERTIES OF HYDROPEROXIDES AND THEIR DIMERS

Hydroperoxide	Bond population of O-O bond		$\frac{1}{2}N^{LU\,a)}_{p\sigma}$	Total energy (eV)
	$p\sigma$	total		
H_2O_2	0.349	0.359	−0.309	−309.67
$(H_2O_2)_2$	0.349	0.359	−0.155	−619.30
CH_3OOH	0.346	0.361	−0.309	−413.80
$(CH_3OOH)_2$	0.346	0.361	−0.189	−827.27
C_2H_5OOH	0.345	0.358	−0.308	−517.21
n-C_3H_7OOH	0.345	0.357	−0.308	−620.39
n-C_4H_9OOH	0.345	0.356	−0.308	−723.56
t-C_4H_9OOH	0.343	0.354	−0.306	−722.83
$(t$-$C_4H_9OOH)_2$	0.343	0.356	−0.154	−1442.19
$C_6H_5C(CH_3)_2OOH$	0.342	0.350	−0.143	−1080.21

O···H distance of the dimer was taken to be 1.79 Å.

a) One-electron bond population of the O-O $p\sigma$-orbital in the LU MO.



AO population of S d-orbitals
$d_{z^2}=0.068$ $d_{xy}=0.092$
$d_{xz}=0.142$ $d_{x^2-y^2}=0.092$
$d_{yz}=0.142$

Fig. 3. Electronic structure of $(CH_3)_3SCl$.

position of ROOH. Table 2 lists the experimental data obtained from the decomposition reaction of cumene hydroperoxide. Except for transition metal ions, the order of the ability with regard to the ROOH decomposition (estimated from the amount of the hydroperoxide decomposed) was as follows: triphenylsulfonium chloride $\gg$ diphenylsulfide $>$ triphenylphosphite $>$ trimethylphosphite $>$ triethylphosphite $\simeq$ thiophene. Considering that the ability would be reflected in the AO population of the nonbonding orbital (N_{nbo}) of the central sulfur or phosphorus, in particular, that in the highest occupied (HO) MO ($1/2N^{HO}_{nbo}$), the order of the values of N_{nbo} or $1/2N^{HO}_{nbo}$ listed in Table 3 is in agreement with that of the ability mentioned above. In sulfonium chloride and thiophene, the contribution of the partially-occupied sulfur d-orbitals to the ROOH decomposition should be taken into consideration (this will be discussed, in detail in the later part of this paper).

In regard to the catalytic decomposition of ROOH by the low-valent transition metal ions, the order of the

TABLE 2. ABILITIES OF SULFONIUM COMPOUNDS AND SOME NUCLEOPHILES FOR THE DECOMPOSITION OF CUMENE HYDROPEROXIDE

Compound	Concentration (mol/l)	Temp. (°C)	Time (hr)	CHP decomposed (%)	Products$^{a)}$ (mmol)		
					AP	DCP	CA
None		80	4	4.44	0.24	trace	0.76
$(C_6H_5)_2S$	0.148	80	4	88.90	1.64	2.2	13.8
$(C_6H_5)_2S$	0.216	25	4	trace			
$(C_6H_5)_2S{=}O$	0.48	80	3	trace			
$\overline{CH(CH)_3S}$	0.12	80	3	20.44	4.0	trace	0.6
$\overline{CH(CH)_3S}$	0.476	80	4	69.33	13.6	—	—
$(C_6H_5)_3SCl$	0.141	80	4	96.89	10.63	4.16	1.91
$(C_6H_5)_3SCl$	0.670	55	4	24.44	2.29	1.12	0.45
$(C_6H_5)_3SCl$	0.424	80	5	99.51	13.28	2.77	3.56
$(CH_3O)_3P$	0.148	80	4	39.11	0.88	trace	7.3
$(C_2H_5O)_3P$	0.148	80	4	28.44	1.04	0.34	4.70
$(C_6H_5O)_3P$	0.148	80	4	42.22	1.10	trace	8.25
Ni(II)$^{b)}$	0.006	80	4	27.56	1.38	trace	4.81
Co(II)$^{b)}$	0.006	80	4	100.0	4.73	trace	19.1
Fe(II)$^{c)}$	0.006	80	4	25.33	1.23	trace	4.42

a) Other products such as methane, phenol, sulfoxide, *etc.* were neglected in this table for the sake of simplicity. See Experimental for the abbreviations.

b) Stearates.

c) A naphthenate.

The initial concentration of cumene hydroperoxide was 22.5 mmol.

TABLE 3. AO POPULATION OF THE NONBONDING ORBITALS OF A SULFONIUM COMPOUND AND SOME NUCLEOPHILES

Compound	N_{nbo}	$\frac{1}{2}N_{\mathrm{nbo}}^{\mathrm{HO}}$	HO (nonbonding orbital (eV)
$(CH_3)_2S$	1.993	0.729	−11.98
$(C_6H_5)_2S$	1.845	0.312	−11.74
$\overline{\mathrm{CH(CH)_3S}}$	1.579 (0.064)		−12.49
$(CH_3)_3SCl$	1.981 (0.068)	0.701	−11.42
$(CH_3O)_3P$	1.298	0.197	−12.28
$(C_2H_5O)_3P$	1.231	0.156	−12.06

Values in parentheses stand for the AO populations of the sulfur d_{z^2} orbtal.

ability with regard to the ROOH decomposition: Co(II) > Ni(II) > Fe(II), can be well explained by its parallelism with the energy required for the electron-releasing from the *d*-orbitals of the transition-metal ion to the O–O $p\sigma$-orbital: Co(II) (7.84 eV)[26] > Ni(II) (9.24 eV)[26] > Re(II) (11.00 eV).[27]

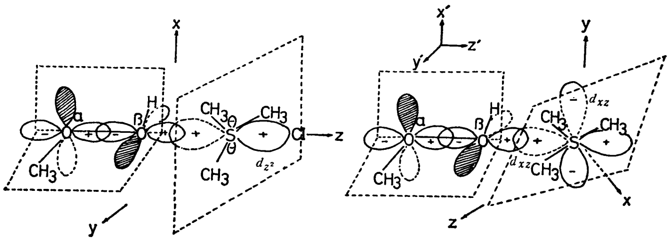
The Interaction between ROOH and the Sulfonium Compound or Some Nucleophiles. First, it is necessary to mention the electronic structure of the sulfonium compound. The ASMO SCF calculations on $(CH_3)_3\cdot SCl$[28] supported the planar C_{3v} symmetrical sulfonium cation and suggested a suitable location of the counter chloride (S–Cl = 3.5 Å) from the energetic point of view. As has already been mentioned, the sulfonium chloride is characterized by its partially-occupied sulfur *d*-orbitals (see Fig. 3), and the remarkable ability of the compound with regard to the ROOH decomposition as compared with those of sulfides or phosphites is the result of the contribution of this sulfur *d*-orbitals (especially, the d_{z^2}-orbital) to the interaction with the LU antibonding O–O $p\sigma$-orbital in ROOH. This is consistent with the change in the values of N_{nbo} and the bond population of the O–O (M_{OO}) recorded in Table 4, where two distinct modes of interaction between CH_3OOH and $(CH_3)_3SCl$, *i.e.*, Type I and Type II, are taken into consideration (see Fig. 4); in Type I, the interaction mainly occurs between the sulfur d_{z^2}-orbital of the former and the O–O $p\sigma$-orbital of the latter, while in Type II, the sulfur d_{xz}-orbital interacts predominantly with the $p\sigma$-orbital. In view of the smaller value of M_{OO} in Type I at S–O_β = 3.0 Å as compared with that of M_{OO} in Type II, the stronger interaction can be expected by Type I. This long-range interaction between CH_3OOH and $(CH_3)_3SCl$ supports the role of the sulfur *d*-orbital in the catalytic decomposition of hydroperoxides, as can be seen from Fig. 5.

TABLE 4. CHANGES IN THE N_{nbo} OF $(CH_3)_3SCl$ AND SOME NUCLEOPHILES AND THE M_{OO} OF CH_3OOH DUE TO THE INTERACTION

Compound	N_{nbo}	M_{OO}
$(CH_3)_2S$	1.993	
$(CH_3O)P$	1.298	0.361
$(CH_3)_3SCl$	1.981	
	(d_{z^2} = 0.068)	
	(d_{xz} = 0.142)	
$(CH_3)_2S$[a]	0.622	0.329
$(CH_3O)_3P$[a]	1.129	0.350
$(CH_3)_3SCl$[b]	1.955	
in Type I	(d_{z^2} = 0.052)	0.249
$(CH_3)_3SCl$[b]	1.501	
in Type II	(d_{xz} = 0.061)	0.266

a) The distance between the O_β in $CH_3O_\alpha O_\beta H$ and the S in $(CH_3)_2S$ (or the P in $(CH_3O)_3P$) was 2.0 Å.

b) The distance between the O_β and the central S was 3.0 Å.



Type I-Interaction Type II-Interaction

Fig. 4. Two distinct interaction between $(CH_3)_3SCl$ and CH_3OOH.

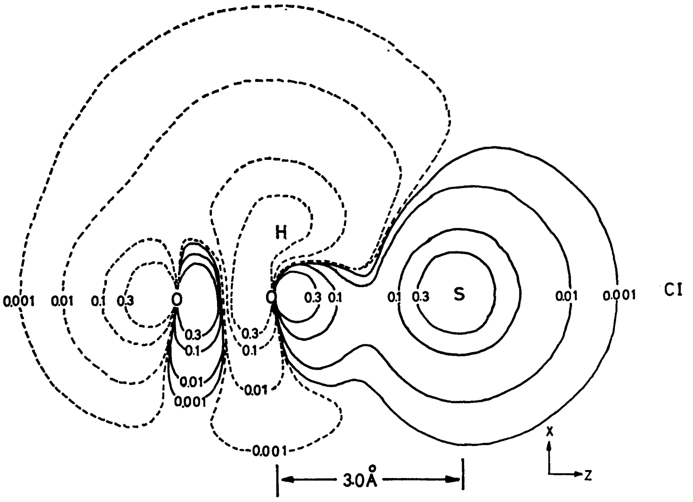


Fig. 5. Orbital contour of LUMO in the long-range interaction between CH_3OOH and $(CH_3)_3SCl$. (the solid and broken lines indicates the positive and negative MO signs, respectively.)

The major portions of the present calculations were carried out on a FACOM 230.60 computer at the Computer Center at Kyushu University while a part of them were done at Kyoto University.

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